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Personal Mass Spectral Data Base in Floppy Disk System

II. Correlations between Mass Spectra and Unsaturation in Hydrocarbons

Yosuji KOYAMA* and Kogaro MAEDA*

(received December 3, 1985)

[illegible]

1. Foreword

With the sudden recent progress in LSI technology there has been a remarkable drop in the price and a remarkable rise in the performance of the microcomputer systems (including some personal computers). Against such background the use of personal data bases using such type of hardware system and aimed at a relatively small number of people has gradually become widespread. Taking as first subject the mass spectral

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data, we built a personal mass spectral data base using a form limited to only the required smallest items with regard to the data format of the recorded compounds. We referred ourselves for the data base to the mass spectral data base compiled by Heller[1] et al. Selecting from this data collection the hydrocarbons only, we completed a data base for 1813 hydrocarbons. We have already reported on the various technical problem points encountered in the actual construction of these data[2]. p. 116 This data base contains the m/z of the base peaks from the mass spectra as well as the 10-13 m/z of the characteristic peaks about 10% higher in the increasing order of ionic strength and expresses at most only the relative sizes in the order of those arrangements.

There are various systems of using and of making the most of such data bases. They seem to vary according to the purposes. In the constructed data base the names of the compounds and their molecular formulae are the information entered about the structure of the compounds. However, the structure formulae themselves are not entered. There seems to be a close relationship between the peaks appearing in the mass spectra and the chemical structure of the molecules. As one way of using this fact, the present report proposes to examine first the correlation between the structural data held mainly by the molecular formulae and the base peaks as well as with the other characteristic peaks. This means that although we knew the degree of unsaturation of the molecules from the various molecular formulae[3], we examined the relationship between the molecular groups of the same unsaturation degree and the peaks appearing from these molecules, and by a very simple statistical treatment were able to elucidate these mutual relationships. It became also evident that the presence of the molecular ion peaks is closely related to the molecular structure. We will hereafter report on these results too.

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2. Base peaks and molecular formulae

2.1 The molecular formulae and the structures of the molecules

Hydrocarbons are molecules made from two elements viz. carbon and hydrogen, and the particular molecules have several different carbon-hydrogen combinations. In order to examine how the hydrogen combines with the basic number of carbon atoms in the hydrocarbons, one expresses the "m" values by the - 2, 0, 2, 4, 6.... even numbers, when the molecular formula is given in the C_nH_{2n-m} form.

The compounds for which "m" is expressed by -2, that is C_nH_{2n+2} are saturated aliphatic hydrocarbons. All these molecules are hydrocarbons that have a chain structure without double or triple bonds.

The compounds for which "m" is 0 are unsaturated aliphatic hydrocarbons with one double bond or saturated alicyclic hydrocarbons (single ring) such as cyclopentane and cyclohexane. These compounds are of an unsaturation degree 1.

Compounds whose molecular formula is C_5H_8, C_6H_{10}, C_7H_{12} and such are expressed by C_n-H_{2n-2} (m = 2) and have 2 double bonds or contain 1 triple bond. There are also unsaturated alicyclic hydrocarbons such as cyclohexene that contain 1 double bond. The unsaturation degree of all compounds is 2.

Furthermore, as "m" increases in the 4, 6, 8.... progression, the number of double and triple bonds increases and the degree of unsaturation rises accordingly. Among the hydrocarbons recorded together in the present data base, the compound with the highest degree of unsaturation was m - octiphenyl $C_{48}H_{34}$ and its "m" value was 62.

The molecular formulae of all hydrocarbons being expressed as a function of "m", Fig. 1 shows the results obtained by investigating their distribution frequencies.

The molecules in which side chains of methyl, ethyl and such are bonded to phenyl radicals are C_nH_{2n-6}. These molecules for which m = 6 were presently the most numerous. There are also many molecules for which "m" ranges -2 to 8. They may represent 78.5% of the totality. Molecules whose "m" is 10 or higher become gradually less common and m < 30 represent about 98.6%. Hexaphenylene $C_{36}H_{24}$ (m = 48) and ovalene $C_{32}H_{14}$ (m = 50) are rare molecules with an extremely high degree of condensation.

It seems that generally there are numerous hyrocarbons whose molecular structure acquires some ring shape when the degree of unsaturation rises. In Fig. 2 we show the results obtained by plotting "m" on the abscissa and by plotting on the ordinate the proportion of ring-shaped compounds with regard to the total number of compounds corresponding to the various particular "m". The results show that about 47% of the ring-shaped molecules (single ring) are located at m = o, that the proportion of ring-shaped molecules increases suddenly at "m" = 2 and higher, and that most molecules of "m" = 8 or higher are ring-shaped. There were 86 compounds at m = 10, but 2, 6, 10, 14, 18, 22 - tetracosahexaene, 2, 6, 10, 15, 19, 23-hexamethyl- $C_{30}H_{50}$ was the sole chain hydrocarbon having 6 double bonds. One might say that this represents an extremely rare case. p. 117

2.2 Correlation between base peak distribution and molecular formula[4)]

The base peak (M_B^+) may be mentioned as being one of the main peaks in the mass spectrum. We have already reported that m/z 43 ($C_3H_7^+$), m/z 57 ($C_4H_9^+$), m/z 55 ($C_4H_7^+$), m/z 41 ($C_3H_5^+$) and such are numerous as base peaks of hydrocarbons.[2)]

We show in Table I the results obtained when examining the correspondence between the 15 upper-level base peaks of such high frequency and the "m" of the molecular formulae (C_nH_{2n-m}).

(1) We see that the base peaks m/z 43 and m/z 57 are overwhelmingly numerous among the saturated aliphatic hydrocarbons (m = -2), that with regard to m/z 43, 108 such hydrocarbons out of a total number of 151 (about 72%) and with regard to m/z 57, 106 out of 122 (about 87%) are represented by C_nH_{2n+2} compounds. Furthermore, among 219 compound excepting methane, ethane, propane from the 222 C_nH_{2n+2} compounds in the present MSDB, the proportion of base peaks being either m/z 43 or m/z 57 reaches the extremely high value of 97.7%. One may say that these 2 peaks were confirmed to be typical base peaks with respect to saturated aliphatic hydrocarbons.

With the base peak m/z 57, there are a few compounds in which "m" is 0, 2, 4, 6 but there are no compounds with a "m" higher than 8. With the present data base, this is the least we can say.

(2) With the base peaks m/z 41, m/z 55, m/z 69, m/z 83, "m" = 0 which means that they appear in the largest number from the C_nH_{2n} compounds. Thereunder, as "m" becomes 2, 4, 6.... the frequency declines largely. However, these base peaks do not appear at all from the saturated aliphatic carbohydrates. For the compounds whose base peaks are m/z 41 and m/z 55, "m" seems to be limited to 8 and under. For the compounds with m/z 83, "m" seems to be limited to 4 and below.

The base peak m/z 56 ($C_4H_8^+$) appears virtually only for compounds with "m" = 0. Yet this base peak appeared in two C_nH_{2n+2} compounds. These results seem to be exceptional and we will explain this later. p. 118

(3) The base peaks m/z 67 ($C_5H_7^+$), m/z 81 ($C_6H_9^+$), m/z 95 ($C_7H_{11}^+$) and such appear frequently with C_nH_{2n-2} compounds. They

appear in small numbers with the compounds whose "m" is 4, 6, 8.... and so on. With the C_nH_{2n+2} and C_nH_{2n} compounds, these base peaks do not appear.

(4) All base peaks m/z 79 ($C_6H_7^+$) appear only with compounds whose "m" is 4. This means that if the base peak is m/z 79, the molecule is likely to be C_nH_{2n-4}. It seems that by examining the presence of the maximum mass m/z, one should be able to predict approximately the size of the molecule. The base peak m/z 93 ($C_7H_9^+$) too seems to appear only with the molecules whose "m" is 4 and 6 and does not appear with molecules at other degrees of unsaturation.

(5) The base peaks m/z 91 ($C_7H_7^+$), m/z 105 ($C_3H_9^+$), m/z 119 ($C_9H_{11}^+$) and such appear often with the C_nH_{2n-6} compounds but decline conspicuously as "m" progresses along 8, 10.... . The two m/z excepting m/z 119 do not appear with the molecules whose "m" is -2, 0, 2, 4.

As we explained, from the above (1) to (5), we see that if we examine the distribution of these 15 base peaks of high frequency and of the particular "m", one may perform a grouping of the m/z having the highest frequencies at the respective "m". On the basis of these results, we examined the relationship between the frequency of all base peaks (195 species) and "m". Among the 195 species of base peaks, there are 53 species of base peak for which there is only one compound such as m/z 16 of methane, m/z 29 of propane and such, and 35 species of base peak for which there are only 2 compounds.

So, there are 88 species of base peaks for which there are only one or two compounds (about 45% of all species of base peaks). However, excepting several species of base peaks, we observed the most numerous "m" with regard to the particular base peaks, and were able to perform

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grouping by the C_n carbon numbers corresponding to the m/z values. The results obtained by consolidating the relationships with "m", m/z, C_n with regard to all base peaks are shown in the Table at the end.

Thus most base peaks are grouped by the particular "m" and C_n. The table shows that the particular base peaks do not appear from the molecules having an unsaturation degree lower than these grouped "m". There was however even if only small also a presence of base peaks indicating a distribution different from these. As Table I shows, the fact that some data are contained in brackets indicates with regard to m/z 56 and m/z 119 that although the groupings at the "m" of the greatest frequency agree basically in accuracy with the other base peaks, both base peaks appear also from molecules with an unsaturation degree inferior to the "m" used for grouping.

As Table II indicates, the base peaks demonstrating such distribution were of 9 species (eleven molecules). In this Table the circled numbers excepting m/z 114 and m/z 174 correspond to the values of "m" showing the largest distribution among the respective m/z. If we consider the relationship between most base peaks and "m", we see that the presence of these 11 base peaks is an extremely rare case. However, we examined the spectra of some of these molecules and made some considerations which we present hereunder.

(a) For octane, 2-cyclohexyl- $C_{14}H_{28}$ and eicosane, 2-cyclohexyl- $C_{26}H_{52}$ the m/z 82 was the base peak. However, with C_nH_{2n} the cases where the ionic strength of m/z 83 was higher than that of m/z 82 in the molecules containing 6-member rings were overwhelmingly more numerous regardless of the size of the side chains.

(b) In the spectrum shown in Fig. 3, the base peak is m/z 147. p. 119 Yet despite the molecular weight of 208, we note the m/z 175, m/z 203

and m/z 218 peaks. If we refer to the spectra of other compounds having similar molecular structures, we estimate

$m/z\,218 \rightarrow 208\ (M^+)$ $\quad m/z\,200 \rightarrow 190\ (M-18)^+$

$m/z\,203 \rightarrow 193\ (M-15)^+$ $\quad m/z\,165 \rightarrow 175\ (M-33)^+$

$m/z\,177 \rightarrow 165\ (M-44)^+$ $\quad m/z\ \ 31 \rightarrow 31$

In short, we see that one may shift in the direction decreasing the scale of the m/z axis by 10 units. Moreover, the presence of these peaks suggests the possibility of compounds which are not simple hydrocarbon substances (containing perhaps oxygen) and it seems that one must reexamine the data.

(c) In the spectra of 1H-cyclobut[a]indene, 2,2a,7,7a-tetrahydro- $C_{11}H_{12}(M_B^+:114)$ the peaks corresponding to m/z 26, m/z 30, m/z 61, m/z 37 appear with relative strength.

(d) Since benzene, 1,4-diethyl, 2,3,5,6-tetramethyl- $C_{14}H_{22}(M_B^+:174)$ has a symmetrical molecular structure m/z 175 $(M-15)^+$ has a relative strength of the 12-13% order and is expected to be noticeably smaller than m/z 174 $(M-16)^+$.

(e) With nephthalene, 1,7-diphenyl - $C_{22}H_{16}$ $(M_B^+:278)$ m/z 278 $(M-2)^+$ is overwhelmingly larger than with $(M-C_6H_5)^+$. Moreover there is virtually no appearance of M^+.

(f) With 1H-3a,7methanoazulene, octahydro-3,6,8,8-tetramethyl-, ...$C_{15}H_{26}(M_B^+:119)$, m/z 204(M-2) shows an ionic strength of about 20%. M^+ does not appear.

(g) With naphthalene, decahydro-1,6-dimethyl-4-(1-methylethyl), didehydro deriv. $C_{15}H_{26}$ the base peak m/z 161 is $(M-45)^+$ and there is a strong appearance of m/z 204 corresponding to $(M-2)^+$. There is practically no appearance of M^+.

As we explained in the above (a)~(g), there appeared to be in the spectral data collected by the presently used MSDB some data

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requiring a reexamination. Yet we made no confirmation with regard to the particular spectra.

As we explained so far, we saw with regard to most base peaks that there was certainly a correspondence with a determined "m". There were however base peaks which did not necessarily fit into these groupings. If one adopts the relationships with "m" that are applicable to most base peaks, then if for the particular standard peaks shown in Table III, the circled particular "m", that is the "m" of m/z 39 and m/z 110 appears most frequently in the molecules 2, the "m" of m/z 44 in the molecules -2, the "m" of m/z 122 and of m/z 135 in the molecules 4, the "m" of m/z 148 in the molecules 6, one obtains results that on the whole are well coordinated. However it could be that in the 6 types of base peak shown here the molecules having the particular circled "m" value were not originally present and that the cause is that as in m/z 135 the frequency was not the greatest. As for this factor, it seems that all base peaks with the presently used MSDB had a low frequency of 1-4. The details however are not known.

Fig. 4 shows the spectrum and structural formulae of the hydrocarbon atoms whose base peak is m/z 44. From the instances of spectra of molecules possessing 7-member rings and resembling the structure of these molecules, one may quite well expect the presence of peaks such as m/z 91, m/z 105, m/z 77. It is however difficult to expect the presence of these ions and a relative strength of 100% if m/z 44 is made to be $C_3H_8^+$. It seems that this is due to the quality of the data but there is no confirmation.

However, none of these base peaks appears from molecules having a "m" that is smaller than that of the particular circled molecules. Essentially there is no molecule escaping the grouping rules of the base

peaks and "m", and one may say that the coordination between the base peaks as a whole and "m" is thoroughly kept.

If we examine the correspondence between the standard peaks and "m", we note the presence of a group of compounds yielding peaks p. 121
corresponding only to the value of a certain unique determined "m". We explained this with regard to m/z 79 in Table I. Table IV shows the relationship between the 10 types of base peaks having a great frequency and the "m" values. One may say that if the base peak is m/z 79, the molecule yielding this spectrum has a "m" of 4 (unsaturation degree: 3). The characteristics of these 28 molecules is that (a) all chain-form molecules are molecular structures containing double and triple bonds, (b) the unsaturated cyclic molecules containing two double bonds are molecules ranging from C_6 to C_8 such as cyclopentadiene and the other molecules with a cyclic structure are molecules having a size of up to C_{12}. There are benzene rings wherein are present together 17 molecules whose base peak is m/z 133, and 8 molecules for which m/z is the base peak.

If the "m" values are limited in this manner, it becomes to a certain extent possible to estimate the structure of those molecules and it seems that useful clues are provided toward the study of compounds.

3. Total peaks and molecular formulae

3.1 Correlation between total peak distribution and molecular formulae[5)]

The number of fragment peaks appearing in the mass spectrum differs according to the particular molecules. Even for molecules with a molecular weight of 1,000 or less, the number may be 500-700. It seems however that the ionic strength of these peaks is often about 10-20% lower. In the present data base the relative strength is about

10% higher and no peaks smaller than the 10-13 position are entered. The data base was built upon such restrictions and we examined the frequency distribution of all the recorded peaks. From m/z 13 (CH^+) to m/z 612 there are about 17,000 such peaks, Table V shows the results obtained when examining the correspondence between the 15 peaks of great frequency and "m".

(1) In the total peak distribution including the base peaks, the most abundant peak was m/z 41 ($C_3H_5^+$). It appears with 1172 molecules, corresponding to about 65% of the total hydrocarbons. We discovered that with saturated aliphatic hydrocarbons that are C_nH_{2n+2} out of 220 molecules excepting methane and ethane (in every case the molecular weight is below 41), m/z 41 appears from 219 molecules excepting 1 molecule. The molecule for which no m/z 41 appeared was octadecane, 2,2,4,15,17,17-hexamethyl-7,12-bis(3,5,5-trimethylhexyl)-$C_{42}H_{86}$. It was a molecule showing singular spectra such that expecting for the base peak m/z 57 the relative strength of all other peaks was 10% lower. However we noted a presence of m/z 41 together with m/z 56, m/z 71 in the mode of several % peaks.

With the C_nH_{2n} molecules m/z 41 appears from 277 molecules out of 280 molecules excepting ethene, and with the C_nH_{2n-2} molecules from 274 molecules out of 281 molecules excepting excepting ethylene and such. One may say that with the molecules whose unsaturation degree is 0-2 the probability of m/z 41 appearance is extremely high. p. 122

The next most frequent peak is m/z 55 and appears in about 50% of the total hydrocarbons. More particularly with the C_nH_{2n} molecules m/z 55 appears for 272 molecules amounting to about 98% of the 278 molecules excepting 1-propene and the like. It is a peak appearing

with the same extremely high probability as m/z 41. Otherwise, m/z 27, m/z 39, and m/z 69 which do not appear as base peaks were more abundant fragment peaks than m/z 57 which was abundant in the base peak distribution.

(2) With the saturated aliphatic hydrocarbons the m/z 41 as well as the m/z 43 and m/z 57 peaks too appear for most molecules. There were 4 molecules with a 10% lower m/z 43 and 6 molecules with a 10% lower m/z 57. Except for octadecane, 5, 14-dibutyl $C_{26}H_{54}$ all latter 6 molecules were limited to molecules smaller than C_7H_{16}. One may say that with molecules of C_8 and higher, the probability of m/z 57 appearance is roughly 100%.

Among the saturated aliphatics m/z 43, m/z 57 and m/z 71 are most numerous. All m/z 41, m/z 55, m/z 56, m/z 69, m/z 83 are most numerous in the C_nH_{2n} molecules. Furthermore, peaks such as m/z 67 m/z 81, m/z 95 appear most abundantly in those molecules whose "m" is 2. Yet these peaks do not appear in the saturated aliphatic groups. M/z 91 is abundant for the molecules with an m of "6". It appears also for the molecules with an "m" of 4 but m/z 91 does certainly not appear from molecules with an "m" of 2 or smaller, that is in molecules whose unsaturation degree is 0-2. As to the question of the "m" molecules for which these fragment peaks were most abundant, there is except for m/z 29 and m/z 39 agreement with the "m" numerous in the base peaks obtained in Chapter 2.2. That is, all base peaks such as m/z 41, m/z 55, m/z 56, m/z 69 and total peaks appear most abundantly from the C_nH_{2n} molecules. The m/z 67, m/z 81, m/z 95 peaks together with both the base and total peaks are most abundant with the molecules having a "m" of 2. One may say that this confirms that the "m" groupings in the base peaks may be applied without any change to the total peaks.

There were about 380 types of total peaks and we examined the relationship between about 130 types of peak (from m/z 38 to m/z 207) appearing in hydrocarbons with a frequency of 17-18 or higher on the one hand and "m" on the other. These peaks coincide largely with the groupings of "m" in the base peaks but it seems that the distribution of the peaks may be divided into 3 cases. These relationships are explained through the examples in Table VI.

(1) M/z 50 ($C_4H_2^+$), m/z 92 ($C_7H_8^+$), m/z 134 ($C_{10}H_{14}^+$) and such appear as base peaks. They are always abundant when "m" is 6 and do not appear in those molecules whose "m" is below 4. That is, one may say that if these 3 peaks are base peaks, the molecules have a "m" > 6 (unsaturation degree: 4 or higher). The molecules whose m/z 134 appears as 10% higher peaks (including the base peaks) have indeed m > 6. One may in other words say that if m/z 134 appears as a peak 10% higher, the unsaturation degree of the molecule is 4 or higher.

(2) Those molecules whose m/z 92 appears as a peak other than a base peak are also present as molecules with a "m" of 4. So if m/z 92 is a base peak, one may say that the molecules has m > 6. If it appears as a peak 10% higher other than a base peak, one may say that the molecule has at least m > 4.

(3) The molecules with which m/z 50 appears as a peak about 10% higher other than the base peak appear also from the C_nH_{2n-2} molecules whose unsaturation degree is by 2 lower than the grouped "m" 6. One may say at least that if m/z 50 appears, the molecule has m > 2. p. 123

One may thus consider 3 cases with regard to the unsaturation degree of the molecules whose particular peaks appear. However, cases such as m/z 50 referred to in (3) are extremely rare and the

characteristics appear only in the 4 peaks m/z 39, m/z 77 ($C_6H_5^+$), m/z 127 ($C_{10}H_8^+$) including m/z 50. Excepting these instances of (3) most peaks are cases like m/z 134 either not appearing with molecules of an unsaturation degree smaller than the grouped "m" of (a) or not appearing with molecules with an unsaturation degree smaller by 2 than the "m" grouped as in m/z 92 of (b). The types of peak belonging to (a) and (b) have rates of the same order.

3.2 Estimating the degree of unsaturation from the all-peaks

Excepting the cases where the base peak is m/z 43 and m/z 57 and the like, we explained in 2.2 that the degree of unsaturation of the molecules is limited from the presence of the other base peaks. We also demonstrated in 3.1 from the correlation between the peaks about 10% higher and "m" that the presence of the particular peaks restricts in a certain measure the unsaturation degree of the molecules. On the basis of the results obtained from the relationship between these base peaks and "m", we may expect that it will be possible to estimate with more certainty the unsaturation degree of the molecules by studying the relationship between the all-peaks and "m". Table VIII shows examples of application to molecules in which it was possible to estimate the "m" (correspondence to the unsaturation degree) values of these molecules.

When extracting the peaks in order of increasing ionic strength from the spectrum of benzene, (2-decyldodecyl), the base peak was m/z 43. As the base peak is m/z 43, we know only that "m" is greater than -2. So if watching the other peaks, one applies the results obtained in 3.1, we know that:

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That is, it seems that probably the "m" of the molecule is 6 (unsaturation degree: 4). The molecular formula is $C_{28}H_{50}$ and this determination was correct.

Thereafter, from the spectrum of phenanthrene, tetrahydro- we know:

from the presence of the base peak m/z 41	m > 0
from the presence of m/z 79, m/z 95	m > 2
from the presence of m/z 121, m/z 135, m/z 192	m > 4

As the molecular formula is $C_{14}H_{24}$ we were able to estimate that "m" was 4, that is a molecule of the unsaturation degree 3.

From the presence of the fragment peak m/z 143 with benzene, 3-heptynyl we estimated that the molecule had an "m" of 10 (unsaturation degree: 6).

We examined with regard to the molecules with the frequently appearing 5 upper-position types of base standard the extent to which it was possible to estimate the "m" values.

The results are shown in Table VIII. Aside from the saturated aliphatic hydrocarbons, there were 43 molecules from which m/z 43 was the base standard. Within these 42 molecules*, there were 28 (about 67%) whose "m" value could be estimated from the presence of peaks about 10% higher. For the remaining 14 molecules, we estimated values smaller than the actual unsaturation degree. Among these, 10 molecules were unsaturated chain-form hydrocarbons including 1 double bond.

Out of 97 molecules for which m/z 41 was the base peak there was 47 molecules in which there occurred an m > 2 limitation. For 41 of the p. 124

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*The base of chrysene, 5-methyl-$C_{19}H_{14}$ is m/z 43 but we excepted this molecule as there was a presence of m/z 307 $(M + 65)^+$ and m/z 308 $(M + 66)^+$

47 molecules, we were able to estimate the "m" value. With regard to those molecules whose base peaks were m/z 55, m/z 57 and m/z 91, we discovered the possibility of estimating the unsaturation degree with a high probability.

Among the 566 molecules for which these 5 base peaks appear there were only 47 molecules the unsaturation degree of which we were not able to estimate correctly.

One may say that it was possible to estimate the unsaturation degree of about 92% of the molecules. One may also say that the results suggested that it was possible to estimate with a high probability the degree of unsaturation of the molecules from about the data on 10 peaks at most 10% higher.

4. Molecular ion peaks and molecular structure

It seems that whether or not molecular ion peaks (M^+) are present in the numerous peaks appearing in the mass spectra depends on the structure of the molecules. Clarifying the presence of these M^+ would provide useful clues for estimating the composition and size of the molecules.

4.1 Distribution of the molecular ion peaks of the hydrocarbons

There were about 1180 (about 65%) molecules in the total hydrocarbons (1983 hydrocarbons) whose molecular ions had a relative strength about 10% higher. In order to examine to what extent the molecules for which these M^+ appear characteristically are unsaturated, we plotted the proportion of M^+ appearance for the molecules of every "m". The results are shown in Fig. 5.

In the saturated aliphatic groups, the molecules in which molecular ions appear with relative strength are only 6 going from methane to butane. Among the molecules larger than C_8, it seems that even if M^+ appears, it ends up being 10% lower. As "m" increases along 0, 2, 4 the probability of M^+ appearance increases. At a 12% higher "m", molecular ions appear from almost all molecules. Yet with the molecules whose "m" is 14, 22, 24, 30, the probability of M^+ appearance is smaller than otherwise.

(1) There are 43 molecules with an "m" of 14. Among these, there are 9 condensed polycyclical compounds having a symmetrical molecular structure such as bi-2,4,6 cycloheptatrien-1-yl and benzene, 1,1'-tetradecylidene-bis.

(2) There are 24 molecules whose "m" is 22 and there were 7 molecules whose M^+ was 10% lower. Among these, 5 molecules had a structure such that Me, Et, $CHMe_2$, CMe_3, CH_2CMe_3 side chains were respectively joined to the partial structure held in common with Ph_3C-. There were also molecules in which three $Ph(CH_2)_3$ and one hydrogen were combined with $PhCH_2CHPh_2$ and carbon as centers. The probability that all molecules escape the phenyl base is expected to be high.

(3) There are 20 molecules whose "m" is 24 and 19 molecules whose "m" is 30. There were 3 molecules each with a 10% lower M^+. p. 125 Among these, 4 molecules indeed had in common a partial Ph_3C- structure and they were combinations of these and of $H_2C = CHCH_2$, $PhCH_2$, $Ph(CH_2)_2$, C_6H_{11} (6-term cycles). The others were $Ph_2CH(CH_2)_4\ CPh_2$ molecules and molecules in which $= CH(CH_2)_2Ph$ was bonded with two $(CH_2)_3Ph$, with carbon as the center.

These results suggest that among the molecules with a high unsaturation degree there appear common partial structures in those

molecular groups where molecular ions do not appear strongly. With benzene, 1', 1'', 1'''(1-propyn-1-yl-3-ylidene)tetrakis(PhC = $CCPh_3$) the molecular ion peaks are base peaks. In the molecules whose structural formula is CPh_4, the relative strength of M^+ was about 30%. However in the case of structural formulae with a partial structure having Ph_3CCH- or Ph_3CCH_2-, it seems that often the molecular ion peaks become small in the end.

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4.2 Molecular ion peaks and base peaks

Among the 1180 molecules whose molecular ion peak is about 10% higher, there were 266 molecules whose M^+ was the base peak (M_B^+). Among these, there were 24 molecules with a chain form going from methane to 2-hexane. There are 417 chain-shaped molecules larger than C_7 but there were no molecules in which M^+ was the base peak. There were 96 C_7 molecules ($C_7H_8 \sim C_7H_{16}$) but they were fragment peaks for which all base peaks were other than M^+.

(1) Even if there are no molecules having no side chain at all such as Me, Et and $(CH_2)_n$ among the monocyclic hydrocarbons or cross-linked ring system hydrocarbons (excluding the atoms containing bicyclo ... and unsaturated bonds), there are not so many molecules for which M^+ is the base peak. Among the molecules whose "m" is 0 (C_nH_{2n}) there were 2 cyclopropane among the molecules whose "m" is 2, there were 2 naphthalene, decahydro-, trans, among the molecules whose "m" is 6, there were 2 pyrene, hexadecahydro and chrysene, octahydro-, and among the molecules whose "m" is 8, only perylene, eicosahydro were molecules whose molecular ion peak was the base peak.

(2) Unlike this, there were not too many molecules among the molecules with side chains in the cyclic molecules of (1) whose M^+ was

the base peak. There were eight viz. androstane, D-homoandrostane, (5α)-, 5α-cholestane, 4-methylene and D:A-friedooleanane and such. All these are typical molecules having a steroid carbon skeleton.

(3) Numerous benzene derivatives have been recorded. A strong M^+ appears in almost all molecules. There are however few molecules whose M^+ is a base peak. They were 18 going from benzene to benzene, 3-ethyl-1,2,4,5-tetramethyl - $C_{12}H_{18}$. To explain the characteristics of the structures of these molecules we examined the types of side chain and the numbers of C-C bonds. Table IX shows 17 of these. The molecules having a triple bond are only benzene, ethynyl-. Only benzene, 3-ethyl-1,2,4,5-tetraethyl are molecules with a structure containing no double bond in the side chain. We observed no larger molecules. Although not shown in this Table IX, benzene, 1-cyclobuten-1-yl with unsaturated 4-member ring combinations in the phenyl radicals also have a M^+ that is a base peak. All other molecules have only vinyl radicals or isopropenyl radicals or seem to be limited to cases of presence together with the methyl radicals. In the combinations of ethyl radicals and propyl radicals and such peaks other than M^+ are finally the base peaks. However, benzene, 1-ethynyl-2-methyl- and benzene, 2-ethenyl-1, 3-dimethyl are only vinyl radicals and methyl radicals structures but the base peaks are $(M-1)^+$ and $(M-15)^+$. Both are structures in which methyl radicals combine with neighboring carbon to which are attached vinyl radicals. At the present time, we have no detailed knowledge of the cleavage mechanism of these molecules.

4.3 Molecular ion peaks and molecular formulae[6)]

We explained in 4.2 the molecules (there are 266) whose M^+ is the base peak. There are however 259 molecules whose M^+ is a large peak

of a relative strength coming after that of the base peak. We examined p. 126 the relationship between the carbon numbers of both types of molecules (there are 525) and the hydrogen numbers. From $C_{10}H_8$ to $C_{10}H_{22}$ there are 188 recorded C_{10} molecules but for both types of $C_{10}H_8$ molecules (naphthalene and azulene) M^+ becomes M_B^+. Among the $C_{10}H_{10}$ molecules, M^+ becomes M_B^+ for seven molecules such as benzene, (diethenyl). With benzene, (cyclopropylidenemethyl)-M_B^+ is $(M - 1)^+$ and M^+ was a peak of a 2nd relative-strength position. Among the 20 $C_{10}H_{12}$ molecules, there are 16 molecules whose M^+ becomes M_B^+. The M^+ of the remaining 4 molecules have a relative strength at or below the 3rd position. Thus with C_{10} the M^+ of all $C_{10}H_8$ if M_B^+, that of $C_{10}H_{10}$ is M_B^+ or the second greatest peak. Plotting the carbon numbers on the abscissa and the numbers of combining hydrogens on the ordinate, we examined the presence of M^+ for each molecule of the same molecular formula from CH_4 to $C_{28}H_{58}$. For each molecule we indicated by ○ that M^+ is M_B^+ and by ⊙ that M^+ is M_B^+ or the second largest peak. We showed the results in Fig. 6.

If from C_3 to C_7 the number of hydrogens is below 6, it is extremely likely that the relative strength of M^+ of the molecule is within the 2nd position. One may say with regard to the molecules from C_8 to C_{12} having a hydrogen number of 10 or less, with regard to the molecules from C_{13} to C_{17} having a hydrogen number of 14 or less, with regard to the molecules from C_{18} to C_{22} having a hydrogen number of 18 or less that there is a general relationship such that the hydrogen number increase by 4 at a time in the groups whose carbon numbers change each time by 5, with C_3 as a basis. However not all M^+ of the molecules (7 types, 40 molecules) from A($C_{14}H_{14}$) to G($C_{26}H_{22}$) in the Figure have

necessarily a strength that is within the 2nd position. The 2 bi-1,3,5-cycloheptatrien-1-yl and bi-2,4,6-cycloheptatrien-1-yl molecules out of the 10 $C_{14}H_{14}$ (A) molecules, the 2 benzene, 1,1',1''-(1-ethanyl-2-ylidene) tris and benzene, 1,1',1''-ethylidenetris molecules out of the 4 $C_{20}H_{18}$ (D) molecules, and $C_{26}H_{22}$ (G) benzene, 1', 1'',1'''-(1-ethanyl-2-ylidyne) tetrakis, have an M^+ whose ionic strength is several % lower. Moreover, the M^+ of the five $C_{16}H_{14}$ (B) 9,10-ethanoanthrene, 9,10-tetahydro and $C_{18}H_{18}$ (C), $C_{21}H_{18}$ (E), $C_{25}H_{20}$ (F) molecules have M^+ which is observed as being a 10% higher peak but the relative strength was at or below the 3rd position. We discovered that except for these 10 molecules, the M^+ of the 30 others was M_B^+ or a large peak of the 2nd position. Thus with regard to those molecules whose M^+ appears strongly there is a loose relationship. This correlation between C_n and H_m is shown in the Graph.

4.4 Molecules showing no molecular ion peaks

There were 100 molecules for which no M^+ could be confirmed, representing about 5.5% of all hydrocarbons. We examined the spectra in the books to know whether or not M^+ was present and we proceeded by assuming that if an m/z recognized even if only as an extremely small peak agreed with the molecular weight, we would consider it as a M^+ presence. When comparing with the data contained in MT, we seem to be able to confirm a peak if the comparative strength is about 3% higher. If we examined the C_n distribution of the 100 molecules for which no M^+ presence is noted, we see that M^+ is observed in all molecules from C_1 to C_7 and that the molecules for which no M^+ presence could be confirmed were molecules higher than C_8. In these 100 molecules, there were 29 whose base peaks was m/z 57, 22 whose base peaks was m/z 43. The fact

that there are many molecules for which m/z 57 and m/z 43 are base peaks corresponds to the fact that the saturated aliphatic group molecules represents a large number (40 molecules). There are numerous molecules with a relatively small degree of unsaturation "m" ranging from 2 to 6. We discovered that they amounted to about 90%.

There were 45 chain-form molecules. There were only 5 molecules other than the saturated aliphatic groups viz. 1- nonene, 4,6,8-trimethyl and 8-heptadecane, 9-octyl ("m" is o), 1-nonyme and 1-undecyne ("m" is 2), 1,3,6-octatrienne, 3,7-dimethyl-, (E)-("m" is 4). p. 127

The saturated aliphatic group compounds docosane, 5-butyl have a molecular structure in which 3 alkyl groups are combined, with carbon atoms as the center but it seems that with the molecules having a similar molecular structure such as eicosane, 7-hexyl- and tetracosane, 9-octyl-, no M^+ appears. No M^+ presence was noted either with cyclohexane, (2-decyldodecyl)- and such which have attached 6-member rings instead of the alkyl group Me. The molecules in whose structure such carbon atoms and 3 alkyl groups or, instead of Me 5-member rings and 6-member rings are combined are numerous molecules larger than C_{23}. One might say that they are one typical structure of molecules for which the appearance of M^+ is difficult. When we examine the relationship between the peaks of the greatest m/z and the molecular weight in those molecules for which no M^+ appears, we see that the molecules for which a peak larger than $(M - 57)^+$ appears account for about 90%.

The greatest m/z in the benzene, (1-ethyloctadecyl)- spectrum was 287 ($C_{21}H_{35}^+$). However, the data sheet is not recorded from m/z 301 to m/z 450 in the book-form MSDB[1)]. One may imagine that the data of this range were omitted because there were no m/z larger than

m/z 301. Consequently, it would be normal if the presence of the molecular ions (m/z 358) of these molecules was not confirmed and if the molecules were treated here like molecules for which no M^+ appears. Among the 100 molecules for which there was no M^+ presence, there were about 30 molecules with no spectrum recorded up to the molecular weight. So, although it is impossible to determine immediately whether all these 100 molecules are molecules for which no M^+ appears, one may foresee that in many cases the probability of molecular ions appearing will be extremely small. Because of this however one might conversely say that among the hydrocarbons as a whole, the molecules for which molecular ions do appear are extremely numerous (M^+ is observed with about 94.5% of the ions).

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5. Conclusion

(1) Using a structured data base of 1813 hydrocarbons, we examined the relationship between the peaks of a strength about 10% higher and the degree of unsaturation, and it was demonstrated that most base peaks are most frequent with molecules of a given unsaturation degree and that they do not appear with molecules with a smaller unsaturation degree. Except for several base peak instances such as m/z 56 and m/z 82, such relationships are obtained. Furthermore, the correlation between all peaks about 10% higher and the degree of unsaturation of the molecules agree with the results obtained through the base peaks. We saw that except for very few peaks such as m/z 39 and m/z 50, they do not appear with molecules having a lower degree of unsaturation or with molecules having a degree of unsaturation smaller than 2. One may say that these results demonstrate at least that to a certain extent it is possible to estimate the degree of unsaturation of

molecules from the 10% higher characteristic peaks. This is explained in section 3.

It seems that the correlation between the obtained peaks and degrees of unsaturation of the molecules may be utilized to examine the quality of the mass spectra data.

(2) Among the hydrocarbons, the molecules for which molecular ions appear are about as many as 94.5%. However with about 65% of the molecules, M^+ appears as a peak about 10% higher. One says that the molecular ions do not appear strongly with the saturated aliphatic hydrocarbons. Yet the molecules for which M^+ is about 10% higher are only a few molecules with a size of up to about C_7. With larger molecules, M^+ is below 10% even if it appears at all.

The molecules for which M^+ is the base peak represent about 15%. Among these all molecules larger than about C_8 have a cyclic structure. To satisfy these conditions in the chain-shaped molecules the main factor is the size of the molecule. When we examine the appearance of M^+ among the molecules having one phenyl radical,

the determination with regard to those molecules for which M^+ is M_B^+ will rest on the type of side chains and on their size rather than on the characteristics of the structure showing the position in the ring at which the side chains are attached.

One wonders if there is some structural characteristic in the molecules for which the molecular ionic peak is the base peak or in those molecules whose relative strength is in the 2nd position. We saw that with regard to the molecules above C_3 the probability of M^+ appearing as M_B^+ and as a 2nd-position peak is high regardless of the

structure in the case of molecules having a determined relationship between the carbon number and the hydrogen number.

6. Final remarks

As explained above, we used a personal mass spectral data base to obtain some information regarding the correspondence between the peak data and the compound structures within the hydrocarbons. In the present study we focussed mainly on the relationship between the peaks and the degrees of unsaturation and explained in general terms the relationship between the molecular ions and the structures. We wish to show later the relationship between the peaks and each particular molecular structure. p. 128

We wish finally to thank Dr. Minoru SAKAI of the Mitsubishi Petrochemical Central Laboratory who gave us much useful advice.

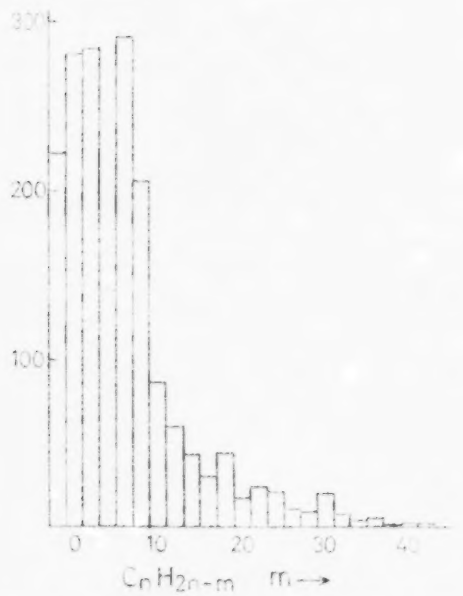

Fig. 1. Abundances of C_nH_{2n-m} compounds with different m-values.

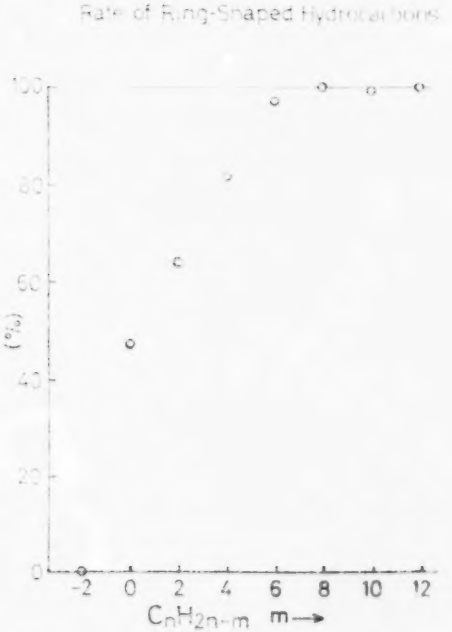

Fig. 2. Rates of ring shaped compounds to C_nH_{2n-m} hydrocarbons with different m values.

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Table I. Numbers of Hydrocarbons with Different m values for the Most Abundant 15 Base Peaks[a]

BASE PEAK		CnH2n-m (m)						
M/z		-2	0	2	4	6	8	10
43	$C_3H_7^+$	108	24	7	1	5	1	2
57	$C_4H_9^+$	106	6	5	1	4		
41	$C_3H_5^+$		50	20	14	8	5	
55	$C_4H_7^+$		72	25	8	2	5	
69	$C_5H_9^+$		26	3	0	2	2	1
83	$C_6H_{11}^+$		24	23	5			
56	$C_4H_8^+$	(2)	42					
67	$C_5H_7^+$			67	2	2	0	0
81	$C_6H_9^+$			44	1	6	2	
95	$C_7H_{11}^+$			27	1	3	0	1
79	$C_6H_7^+$				28			
93	$C_7H_9^+$				28	5		
91	$C_7H_7^+$					62	6	5
105	$C_8H_9^+$					38	3	0
119	$C_9H_{11}^+$				(1)	30	2	0

[a] Largest number for each base peak *m/z* value always exists at each smallest m value, with two exceptions indicated by parentheses.

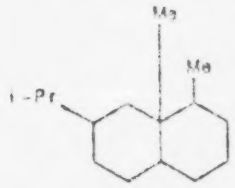
Table II. Nine Base Peak Values of the Exceptions from Table I[a]

Base peak	C_nH_{2n-m} (m)									
m/z	-2	0	2	4	6	8	10	12	28	30
56	2	(42)								
68		1	(10)	5	0	1				
82		2	(4)							
114							1	◯		
119				1	(30)	2				
147			1		(15)					
161				1	(13)					
174					1	◯				
238									1	(2)

[a] Numbers in the circles correspond to the largest numbers in Table I. Total 11 exceptions are all of the exceptions from the m values and base peak relations in Table I. Spectra of these compounds should be examined.

208 $C_{15}H_{28}$ 15404-63-4

Naphthalene, decahydro-1,8a-dimethyl-7-(1-methylethyl)-, [1*R*-(1α,4aβ,7β,8aα)-



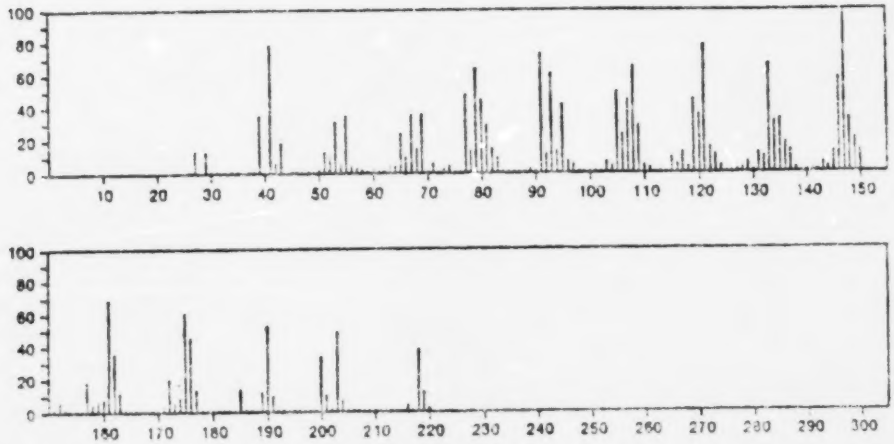


Fig. 3. Mass spectrum of $C_{15}H_{28}$ compound (m = 2) cited in the present NBS/NIH MSDB. Observed base peak is at *m/z* 147.

Table III. Correlations of Hydrocabon Numbers to the Base Peak m/z Value and the m Values[a]

Base peak m/z	C_nH_{2n-m} (m)								
	-2	0	2	4	6	8	10	12	14
39			◯	1	1				
44	◯				1				
110			◯	1					
122				◯		1			
135				(1)	2	1			
148					◯				1

[a] Circles indicate the positions for the largest populations to be expected from the rules in Table I. At present no citation in the MSDB used for the six m/z values and m values.

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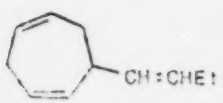
115 $C_{11}H_{16}$ 33156-92-2

1,4-Cycloheptadiene, 6-(1-butenyl)-, (*S*-(*Z*))



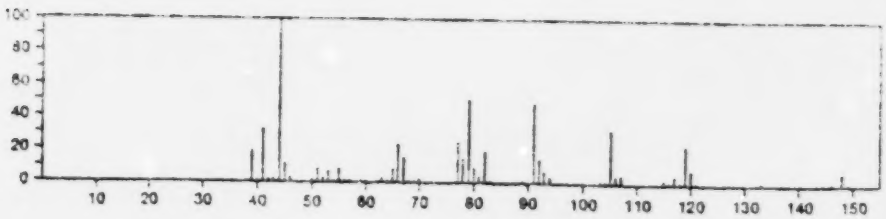


Fig. 1. Mass spectrum of $C_{11}H_{16}$ (m=6). Observerd base peak is at m/z 44.

Table IV. Correlations of Hydrocarbon Numbers to the Base Peak *m/z* Values and the n values[a]

Base peak	C_nH_{2n-m} (n)					
m/z	0	2	4	6	8	10
79	6					
105		9				
79			28			
143				17		
179				8		
117					21	
118					9	
135					21	
141						8
157						13

[a] Hydrocarbons giving these *m/z* values for base peak always correspond to C_nH_{2n-m} with only one n value.

Table V. Most Abundant 15 *m/z* Values for All Peaks Including Base Peaks and their Corresponding Total Numbers[a]

All peak	C_nH_{2n-m} (n)							
M/z	No.	2	3	4	5	6	7	8
41 $C_3H_5^+$ 41	1	278	478	474	630	905	774	410
55 $C_4H_7^+$ 55	2	72	273	234	62	79	57	54
69 $C_5H_9^+$ 69	3	68	167	205	155	97	50	16
43 $C_3H_7^+$ 43	4	215	532	85	50	79	30	8
97 $C_7H_{13}^+$ 97	5	116	178	173	97	67	23	7
83 $C_6H_{11}^+$ 83	6	67	240	114	20	19	7	10
57 $C_4H_9^+$ 57	7	219	147	52	7	53	27	3
29 $C_2H_5^+$ 29	8	139	378	93	23	38	16	2
67 $C_5H_7^+$ 67	9	13	53	204	78	9	17	4
71 $C_5H_{11}^+$ 71	10			5	27	28	10	1
81 $C_6H_9^+$ 81	11			16	7	3	11	2
95 $C_7H_{11}^+$ 95	12	30	153	81			1	
109 $C_8H_{13}^+$ 109	13		4	52		47	10	3
77 $C_6H_5^+$ 77	14	107	116	6		13	2	1

[a] Relations between *m/z* values and n values are also presented as well as for the base peaks in Table I.

Table VI. Relations between Base Peaks, All Peaks and n values for Three *m/z* Values shown in the Largest Populations, at the Case n = 6[a]

		C_nH_{2n-m} (m)					
		0	2	4	(6)	8	10
m/z 50	Base peak				1		
	All peak		8	15	10	4	5
m/z 92	Base peak				10	3	2
	All peak			20	53	18	5
m/z 134	Base peak				1	1	
	All peak				41	3	

[a] Table shows typical three types for the n value: the first, no excess distribution from the minimum n value for *m/z* 134 cases; second, one excess for the case of *m/z* 92; third, two excesses for the case of *m/z* 50.

Table VII. Predictions of n values from Observed *m/z* Values[a]

Base peak
43 91 57 41 55 71 85 69 92 83 97 117
m+ 2 4 4 2 1 m≥6

Benzene, 1-decylcyclodecyl-
MW 386 $C_{26}H_{50}$

Base peak
44 135 67 192 81 96 55 39 95 97 79 121
m+ 0 4 4 2 2 1 m≥4

Phenanthrene, tetrahydro-
MW 192 $C_{14}H_{12}$

Base peak
91 129 143 65
m+ 6 8 10 2 m≥10

Benzene, 3-heptynyl-
MW 172 $C_{13}H_{16}$

[a] Right answers could be obtained for the three cases by using the knowledge revealed from Table I to Table VI.

Table VIII. Other Example of the m value Prediction for the 5 Most Abundant Base Peak Values

base peak m/z	C_nH_{2n-m} (m)		m value ○	m value ×
43	m=-2	108, others 42	28	14
57	m=-2	106,	11	5
41	m=0	50,	41	6
55	m=0	32,	26	14
91	m=6	67,	23	8
		393	121	47

Only 47 compounds could not be predicted their m values among total 506 compounds. This corresponds to 92 % prediction rate.

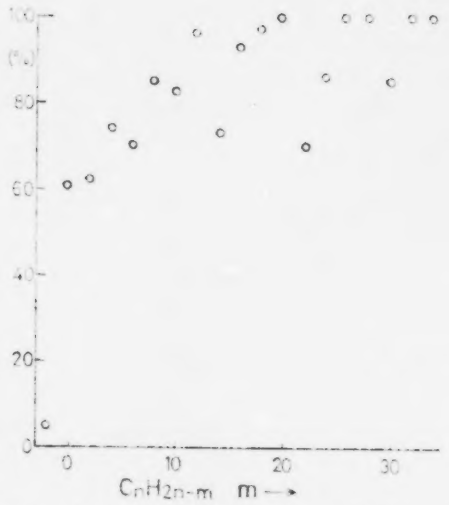


Fig. 5. Rates of compounds giving molecular ion peaks higher than 10 % to the base peaks to C_nH_{2n-m} compounds with diffrent m values.

Table IX. 17 Benzene-Derivatives Giving Molecular Ion Peaks as the Base Peaks, and the Numbers of their Side Chains

Chemical Form		-CHOH	-C=CH₂ H	-C=CH₂ CH₃	-CH₃	-CH₂CH₃
C_7H_8	1	1				
C_8H_8	1		1			
C_8H_{10}	1			1		
	3		1		1	
C_9H_{12}	2		2			
	3		1	1	1	
	3				2	
$C_{10}H_{14}$	2			2		
$C_{10}H_{14}$	3			1	3	
$C_{11}H_{16}$	1				4	1

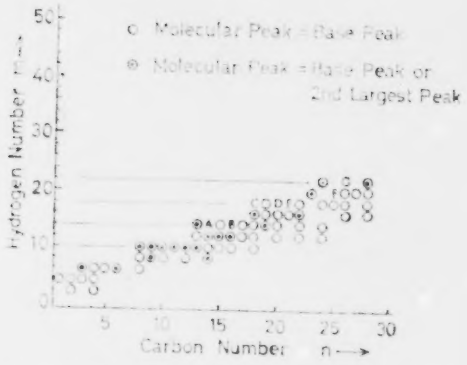
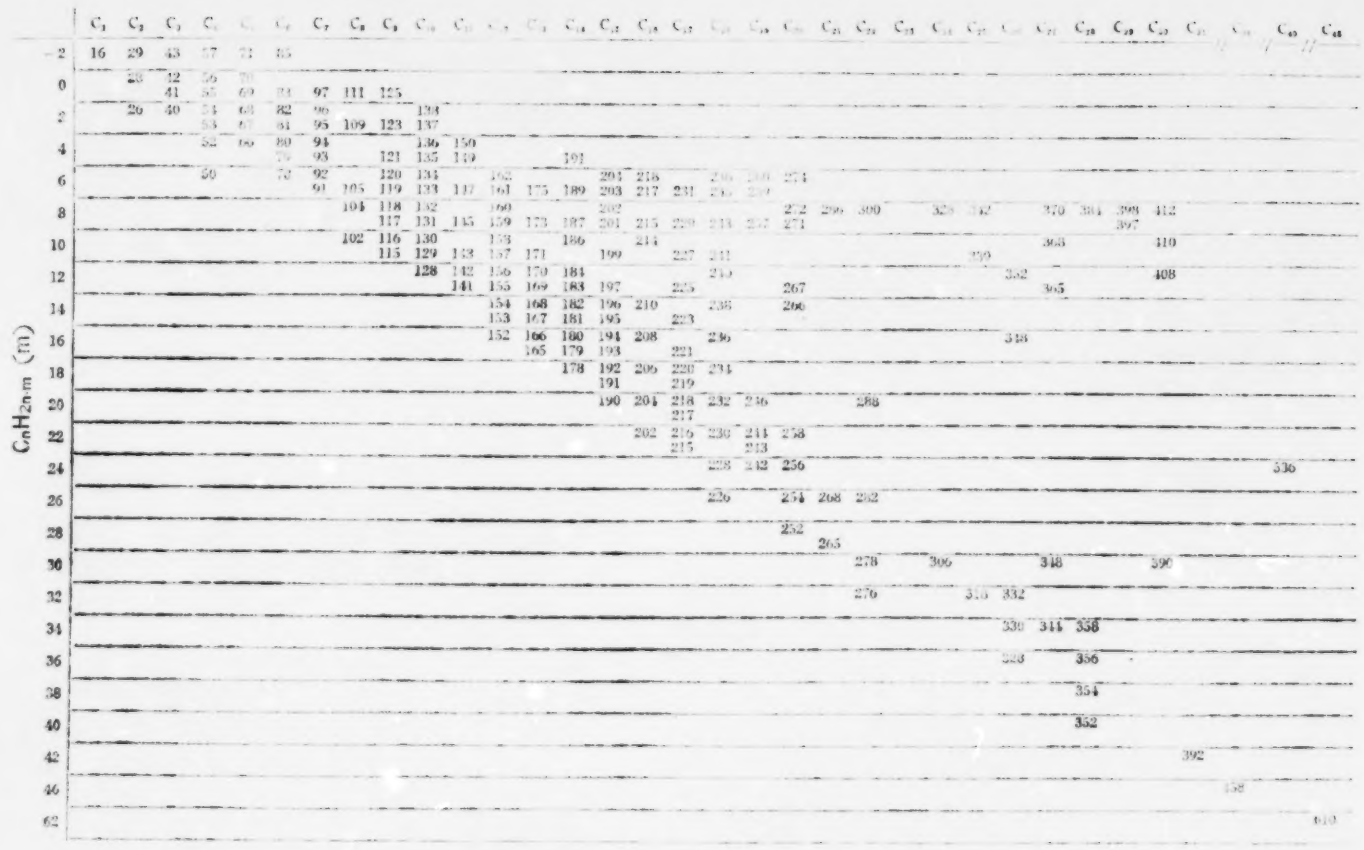


Fig. 6. Correlations between carbon numbers and hydrogen numbers of hydrocarbon compounds giving base peaks and the 2nd largest peaks equal to the molecular ion peaks. Open circles show the existence of the base peaks equal to the molecular ion peaks. Figure indicates that for example, if all hydrocarbons having 17 carbons and 12 to 14 hydrogens always give molecular ions as the base peak, then the open circles are set on the positions. Alphabet A to G show the existence of the combinations of the carbon and hydrogen numbers for the case that all the corresponding compounds do not always give molecular ions as base peaks or 2nd largest peaks.

Appendix Table

Correlation of All Base Peak m/z Values to their Carbon Numbers and also to the n values at which Largest Populations can be seen for the Base Peak Values



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*Translator's note: reading not certain